

Hiroshima Univ.- Fac. of Eng., Farcasanu Ioan Romeo  
 Ehime Prefecture Governmental Office, Mori Takaki  
 Hiroshima Univ.- Fac. of Eng., Yamaguchi Toshiko

## INTRODUCTION

Pesticide transport in soils is influenced by simultaneous processes and properties. Although several models have been developed in order to describe the movement and interactions between solutions and soils particles (van Genuchten and Wagenet, 1989; Kookana *et al.* 1992), difficulties appear in estimating the parameters involved. Adsorption process is often assumed to be fast enough to achieve equilibrium and therefore batch distribution coefficient is commonly used to describe the behavior of pesticide under transport conditions. A comparison of adsorption kinetics studied under both batch and transport conditions can provide a better understanding of adsorption time dependency in soils. The use of First Term Method (FTM) developed by Yamaguchi *et al.* 1989 is an easy and useful method for simultaneous estimation of transport parameters, convective velocity ( $u_0$ ) and hydrodynamic dispersion coefficient ( $D_0$ ), and of retardation factor ( $R$ ) from breakthrough curve (BTC) data. Considering the matter above we tried to determine the influence of soil properties and transport parameters on retardation of pesticides on soils and to compare the distribution coefficients obtained from batch experiments with those obtained from transport conditions using first term method (Yamaguchi *et al.*, 1989) and Parker and van Genuchten' two-site non-equilibrium model (TNE), 1984.

## THEORETICAL PART

The FTM is derived from the analytical solution of the convection-dispersion equation (CDE) which describes the transport of solutes through the soil.

$$R \frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial x^2} - u_0 \frac{\partial c}{\partial x} \quad [1]$$

where,  $c$  is the pesticide concentration in liquid phase ( $\text{mg l}^{-1}$ ),  $D_0$  is dispersion coefficient ( $\text{cm}^2 \text{min}^{-1}$ ),  $u_0$  is convective velocity ( $\text{cm min}^{-1}$ ) and  $x$  is distance (cm). The retardation factor  $R$  (dimensionless) is given as:

$$R = 1 + \frac{\rho k}{\theta} \quad [2]$$

where,  $\rho$  is soil bulk density ( $\text{g cm}^{-3}$ ), and  $\theta$  is volumetric soil-water content ( $\text{cm}^3 \text{cm}^{-3}$ ) and  $k$  is distribution coefficient ( $\text{cm}^3 \text{g}^{-1}$ ). Based on property (III) of the solution for Eq. [1] of BTC pore water velocity ( $u$ ) and dispersion coefficient ( $D$ ) can be determined as:

$$u = \frac{L}{\sqrt{t_1 t_2}}, \quad D = \frac{L^2}{4\xi^2} \left( \frac{1}{\sqrt{t_1}} - \frac{1}{\sqrt{t_2}} \right)^2 \quad [3]$$

where,  $L$  is the length of the column (cm),  $t_1$  and  $t_2$  are time values (min), and  $\xi$  is the value of complementary error function. Initial and boundary condition are the same as given

in Yamaguchi *et al.*, 1989. The relation between  $u_0$  and  $D_0$  of tracers and pesticide  $u$  and  $D$  can be written as:

$$u = \frac{u_0}{R}, \quad D = \frac{D_0}{R} \quad [4]$$

And deriving from Eqs. 3. and 4. the retardation factor can be easily determined as

$$R = \frac{t_T}{t_P} \quad [5]$$

where,  $t_T$  is the retention time in the column for the tracer used and  $t_P$  is the retention time for the pesticide ( $R=1$  for the tracer).

## MATERIALS AND METHODS

Stainless steel micro-columns (25 cm length and 1 cm diameter) were packed with air dry soil to bulk densities of  $1.26 \text{ g cm}^{-3}$  (decomposed granite, 0.425-0.212 mm fraction) and  $1.5 \text{ g cm}^{-3}$  (Hiroshima type, loam soil), respectively. The pesticides used were simazine (2-chloro-4,6-bis(ethylamino)-1,3,5, triazine) and asulam (N-acetyl-p-amino sulphone amide). The pesticide solutions were made in 0.005 M  $\text{CaSO}_4$  and contained  $1 \text{ mg l}^{-1}$  simazine and  $10 \text{ mg l}^{-1}$  asulam.  $\text{D}_2\text{O}$  and  $\text{CaCl}_2$  solutions used as tracers were applied to the soil micro-columns at a constant flow rate ranging from 0.04 to  $0.1 \text{ ml min}^{-1}$  with an HPLC pump (Shimadzu, LC-10AD). Breakthrough curves (BTCs) were monitored with a UV detector (Shimadzu, SPD-10A UV-VIS), and RI detector (Shimadzu, RID-6A) and recorded with Shimadzu, C-R3A recorder. Subsequently, the solutions of pesticide (asulam  $10 \text{ mg l}^{-1}$ , and simazine  $1 \text{ mg l}^{-1}$ ) were applied to the soil columns by shifting quickly the pump from mobile phase (0.005 M  $\text{CaSO}_4$  solution) to the pesticide solution, at the same flow rate of the mobile phase, using a 3 way stopcock. The BTCs of pesticide were monitored in the same way as previously described. Peaks' retention time for pesticides and tracers were measured on HPLC column by direct injections.

## RESULTS AND DISCUSSION

Pore-water velocities and dispersion coefficients estimated from BTC were similar for both tracers ( $\text{D}_2\text{O}$  and  $\text{Cl}^-$ ) used but slightly lower than pore water velocities estimated by the flow rates. This suggested that there were no anion exclusions and no preferential flow ways in our DG or loam packed columns. The sorption data were fitted to the TNE model by a numerical program CNTFIT (Parker and van Genuchten, 1984) and the fractions of "type-1" sites and "type-2" sites and their rate coefficients were computed. A combination of rapid and slow rates of sorption was possible due to the presence of

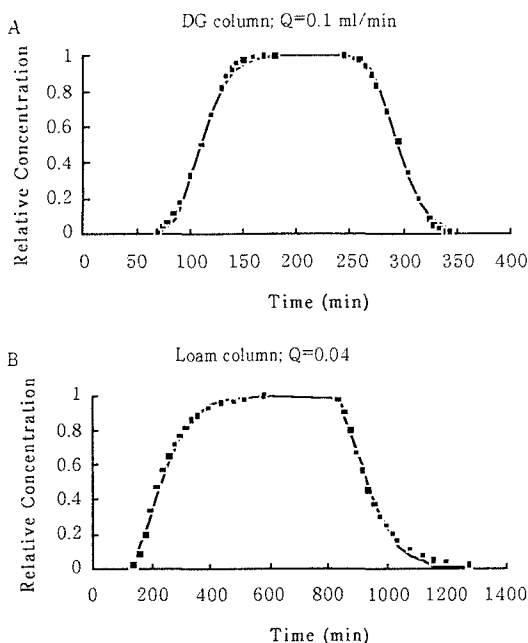


Fig. 1. TNE model fitted to the measured data for asulam ( $10 \text{ mg l}^{-1}$ ) on decomposed granite ( $0.212\text{--}0.425 \text{ mm}$  grain size fraction) and Hiroshima type loam soil.

different type of reaction sites in the soils (organic matter, minerals).

The BTCs of asulam was symmetrical in the case of decomposed granite (Fig. 1.A) but tailing was observed in the case of loam (Fig. 1.B). The values of retardation factor  $R$  estimated using FTM and those from TNE were close in the case  $Q=0.1$  but the differences slightly increased for the lower flow rate ( $Q=0.04$ ).

In the case of simazine, the BTC was almost symmetrical in the DG columns while important tailing appeared in the loam column (Fig. 2. A,B). Simazine much stronger reacted with both types of soil than asulam and the differences between retardation factor of simazine obtained from batch and transport conditions were more significant.

## CONCLUSIONS

The values of pesticide pore water velocities estimated using FTM and TNE model were similar but significant differences appeared when estimating the dispersion coefficient. These differences were more significant in the case of loam soil, where diffusion into clay matrix appears to be the main rate-limiting factor in the adsorption process. For the well structured DG, the extremely low clay mineral content ( $0.4\%$  kaolinite) did not significantly influence the diffusion coefficient and the adsorption process proceeded much faster than in the case of loam soil. Several other works have found that the organic matter increases equilibration time for

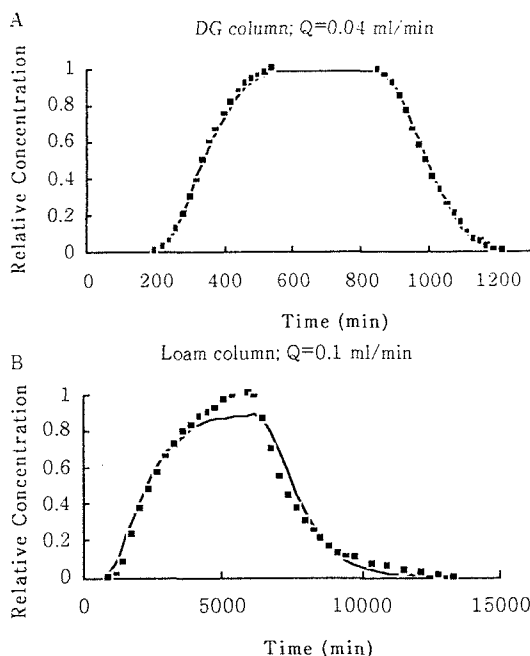


Fig. 2. Breakthrough curves of simazine on decomposed granite and loam soil (TNE model fitted to the measured data).

chemicals in soil (Boesten and van der Pass., 1988.; Kookana *et al.*, 1992). Even if the amount of asulam adsorbed on loam was much lower than that of simazine, their behavior during transport through the soil was similar.

## REFERENCES

1. Boesten, J.J.T.I., and L.J.T. van der Pass. 1988. Modeling sorption/desorption kinetics of pesticides in a soil suspension. *Soil Sci.* 146:221-231.
2. van Genuchten, M.Th., and R.J. Wagenet. 1989. Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* 53:1303-1310.
3. Kookana, R.S., L.A.G. Aylmore, and R.G. Gerritse. 1992. Time-dependent sorption of pesticides during transport in soils, *Soil Science*. 154:214-225.
4. Parker, J.C. and M.Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments, *Bul. of Virginia Polytechnic Inst. and University*, pp.11-17.
5. Yamaguchi, T., P. Moldrup, and S. Yokosi. 1989. Using breakthrough curves for parameter estimation in the convection-dispersion model of solute transport, *Soil Sc. Soc. Am. J.*, 53:1635-1641.